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DEVELOPMENT OF NANOFLUID DETERGENT BASED ON TiO_2 AND PALM OIL-BASED PRIMARY ALKYL SULPHATE

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ABSTRACT

Surfactant is widely known as the main active ingredient of detergent. It derived from petrochemicals that are toxic and non-renewable. Its lack of performance to remove dirt due to random distribution of surfactant is also the limitation of conventional surfactant. Therefore, the necessity of developing detergent based on environmental-friendly surfactant and good dispersing agent effectively rises. Palm-based Primary Alkyl Sulphate (PalmPAS) is a surfactant derived from palm oil that can potentially replace the existing surfactant due to its non-toxic and renewable characteristic. TiO_2 nanoparticle is widely known as a hydrophobic material that can be turned into a hydrophilic when exposed to photon/light source. It is also expected to be a good surfactant dispersing agent without altering the surfactant performance. In addition, TiO_2 can produce powerful oxidizing species which can degrade organic pollutants, including dirt. The aim of the present study is to discuss the PalmPAS-TiO_2 detergent formulation that is expected to effectively remove dirt and degrade the leftover waste. The methods of the research are synthesis of PalmPAS-TiO_2 detergent, PalmPAS and TiO_2 stability test by MBAS method and UV-Vis Spectrophotometer, and detergent performance (detergency). Performance testing analysis of the detergent consists of dirt/Methylene Blue (MB) removal and PalmPAS degradation/leftover waste analysis using UV-Vis Spectrophotometer. PalmPAS-TiO_2 concentration that has been synthesized was 0.1, 0.2, to 0.5% of PalmPAS with specific concentration of TiO_2. In terms of stability, all concentrations showed good stability. PalmPAS concentration that decreased was less than 2% during 14 days of storage while the precipitation of TiO_2 in the detergent is less than 1% after 3 hours being synthesized. MB removal performance of detergent reached optimum conditions on the composition of 0.4% PalmPAS. Detergency on the cloth reached 93% by stirring the cloth using magnetic stirrer while it only reached 84% if the cloth was washed by soaking.

KEYWORDS: Detergent; Methylene Blue; TiO_2; PalmPAS.

INTRODUCTION:
Detergent is a household product used to remove dirt and oil from clothes. Detergent ingredient generally comprises six groups of substances: surfactants, builders, enzymes, bleaching agents, fillers, and other minor additives (Karsa, 1999). Surfactant is the primary ingredients in detergent comprising from 15% to 40% of the total detergent formulation (Tangxin, 2008). However, surfactants that are widely used in commercial detergents derived from petrochemical feedstocks are *non-renewable* and toxic (Benvegnu, 2008). Moreover, there is a lack of effective performance of the surfactant in lifting dirt from clothing due to random distribution of surfactants in detergents when being used (Lara-Martin, 2014). Furthermore, the dirt and surfactant in the leftover waste degraded, but release directly to the environment and pollute it. The example of surfactants, used by commercial detergents, are *Sodium Lauryl Sulfate* (SLS), *Sodium Laureth Sulfate* (SLES) and *Linear Alkylbenzene Sulfonate* (LAS), which are toxic to the human body and the environment (Mungray, 2009). Until now, the existing detergents of Indonesia have not used surfactant that is derived from natural materials or renewable raw materials (Ristiana, 2010).

Surfactants derived from renewable raw materials are characterized by their positive impact on the environment, biodegradability, low or non-toxicity, and innocuousness for human health. In addition, the use of renewables in surfactant production can contribute to save fossil resources, such as crude oil and natural gas, and to the reduction of fossil carbon dioxide emissions (CO_2) and hence could be part of a strategy to mitigate the green house effect. *Palm Oil-Based Primary Alkyl Sulphate* or *PalmPAS is* a surfactant derived from coconut oil. *PalmPAS* have a straight chain from C8 to C18 where the most composition comes from C12 and C14 comprising up to 66% in total. *PalmPAS* itself is environmentally friendly and rarely used as surfactants in detergent (Richards, 2009).

Photocatalyst is a reduction-oxidation process that occurs simultaneously on a semiconductor material when exposed to photons. This process is capable of producing very reactive OH• radical species that can degrade organic compounds in the semiconductor (Mozia, 2010). One of semiconductor material that is often used because it is stable and non-toxic is TiO_2. Al-Qaim (2009) has observed that TiO_2 can degrade *methyl orange* to 99% under sunlight exposure. TiO_2 actually has nano size but still in aggregate form at the start of the synthesis. This led to the formation of two phases at the beginning of the synthesis of detergents, solid phase of TiO_2 and liquid phase of surfactant and water (Chang, 2010). However, Ghamidi (2013) has conducted a treatment to break the aggregate of TiO_2, so that the particle size is reduced to below 100nm by doing sonication and pH adjustment to create nanofluids system. This system causes the TiO_2 stable in the liquid phase and not precipitated or stable after synthesis.

Combination of *PalmPAS* and TiO_2 is expected to produce highly effective detergent that has less dirt and surfactant in leftover waste. Sinha (2009) worked on enhancement between the TiO_2 as a photocatalyst and synthetic surfactant SDS to degrade organic compounds. The results showed that the addition of surfactant can improve the performance of photocatalyst to degrade organic compounds. This paper will discuss the research that combines TiO_2 and *PalmPAS* as detergents. Variations of *PalmPAS* and TiO_2 in nanofluids system will be discussed. Detergent stability analysis consists of TiO_2 and *PalmPAS* stability. Test performance of the detergent is dirt removal tests, as well as dirt and *PalmPAS* degradation test.

MATERIALS AND METHODS:
Synthesis of the detergent began by mixing PalmPAS and TiO_2 in water with variation of composition. The mixture was then stirred and the pH was also adjusted. After synthesis, the detergent stability would be analyzed.

Detergent stability analysis consists of two tests: stability of PalmPAS and TiO_2 in the detergent. PalmPAS stability was observed by measuring the concentration PalmPAS after several days of preparation while the stability of TiO_2 was observed by measuring the rate of precipitation after 3 hours of preparations. PalmPAS concentration was measured using MBAS Method while the rate of precipitation of TiO_2 is analyzed by observing the absorbance of TiO_2 in the detergent using a UV-Vis spectrophotometer.

Performance of detergent consists of detergency, simultaneous system between detergency-degradation, and PalmPAS degradation. The dirt which would be colored on cloth was modeled by MB. Performance of dirt removal or detergency was done by dipping the colored cloth into diluted detergent. After 3 hours, the cloth was lifted and the remaining concentration of MB would be measured. The measurement was done by decolorized remaining MB using chloroform. The concentration of MB was then measured using UV-Vis Spectrophotometer. Simultaneous detergency-degradation was done by dipping and stirring the cloth in diluted detergent under the mercury lamp as a photon source. After 30 minutes, the cloth was lifted and the concentration was then measured using UV- Vis Spectrophotometer. Degradation of PalmPAS was done by measuring the concentration of leftover waste or solution after simultaneous detergency-degradation process. The measurement of PalmPAS concentration was done based on MBAS (Methyelene Blue Active Substance) method.

RESULTS AND DISCUSSION:
Detergent stability is determined by two things that are the stability of TiO_2 and PalmPAS in detergent. The stability of TiO_2 is based on the rate of precipitation of TiO_2 in the detergent. This is because TiO_2 is not soluble in water and will precipitate after several period of time. The stability PalmPAS is analyzed by looking at the changes of its concentration. This is because in the ambient temperature, PalmPAS will tend to precipitate as a result of its straight chain (Richards, 2009). In addition, PalmPAS is an organic compound and expected would be degraded due to the presence of TiO_2 in the detergent (Fujishima, 2000).

Method for examining the stability of TiO_2 and PalmPAS in detergent was spectrophotometer that was adjusted at wavelength of 420 nm. A wavelength of 420 nm was decided to be used in this study as the wavelength of the sulfate white identical with white TiO_2. The absorbance of detergent data can be seen in Table - 1.

Table 1. Absorbance data at λ = 420 nm

PalmPAS (wt%)	Absorbance of Detergent (0 hour)	Absorbance of Detergent (3-Hours)	Absorbance Decrease (%)
0.1	2.920	2.914	00.02
0.2	3.029	3.019	00.03
0.3	3.092	3.090	00.01
0.4	3.092	3.079	00.04
0.5	3.233	3.209	00.07

From Table 1, it can be seen that the decrease of absorbance of detergent in wavelength 420 nm is less than 1% after three hours synthesis. This small decrease in absorbance indicates that the TiO_2 particles can be considered at stable condition. This small precipitation of TiO_2 particles is caused by particles uniformly dispersed with PalmPAS because of pH adjustment and stirring treatment (Lee, 2006).

The decrease of pH causes the surface of the TiO_2 charged with electron that lead to repulsion reaction among the particles of TiO_2. This repulsion causes TiO_2 to be stable and well dispersed in a solution (Jiang, 2002). In addition, stability of TiO_2 is also helped by the presence of anionic surfactant PalmPAS that have hydrophobic and hydrophilic groups at the same time. Hydrophobic group would bind TiO_2 while the hydrophilic group binds with water so that TiO_2 can be more easily dispersed as shown in Figure 1. Therefore, it can be said that the combination of TiO_2 and PalmPAS detergent is stable at this condition.

The stability of PalmPAS was observed by looking at the initial concentration in the detergent from time to time. This was done because PalmPAS at ambient temperature will tend to precipitate. In addition, TiO_2 is a photocatalyst that can degrade organic compounds including PalmPAS.

The measurement of PalmPAS concentration performed with MBAS method. The principle used in MBAS method is MB binds to the anionic surfactant. The bond between the MB and surfactants will be extracted by chloroform. PalmPAS concentration proportionate to the absorbance recorded using spectrophotometer. The concentration of PalmPAS can be seen in Figure 2.

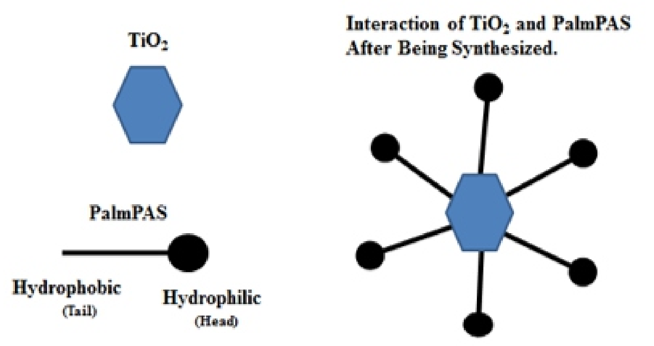

Figure 1. Interaction between TiO_2 and PalmPAS

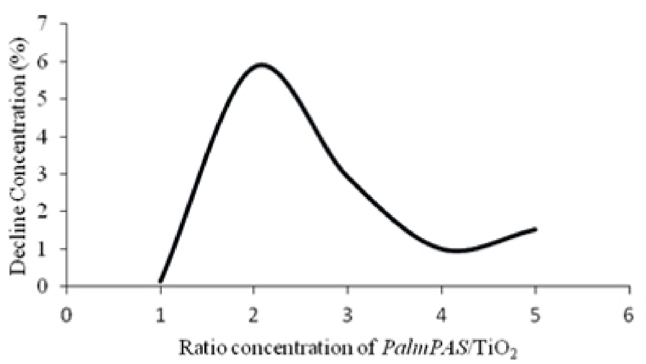

Figure 2. The Decrease of *PalmPAS* concentration after 14 days

From Figure 2, it can be concluded that the concentration of PalmPAS relatively stable for 14 days or hardly degraded and precipitate. The result shows that in a closed container, PalmPAS is not degraded by TiO_2 because photons do not exist to make TiO_2 active in degrading organic compounds. However, on TiO_2 and PalmPAS ratio equal to 1: 2 there was a slight decline more than the other ratios. This is because, in the ratio of 1: 2, surfactants form a micelle for the initial conditions, the groups of surfactant centered the hydrophobic tail. At this point, it is also referred to as CMC (Critical Micelle Concentration) point. At this point, surfactant starts to bind each other so that the concentrations of MB were obtained slightly reduced.

Detergent performance has three analysis to be tested, there are the removal of MB from the clothes (detergency), simultaneous system between detergency and degradation of MB, and degradation of PalmPAS in the leftover waste.

For testing the removal of dirt, clothes that have been colored in MB then dipped into detergent solution for 3 hours. Then, the cloth will be decolorized by chloroform. In the final process, the concentration is analyzed using UV-Vis Spectrophotometer. Variable used to indicate the amount of MB lifted from cloth in a certain period of time called detergency. Figure 3 shows the detergency of dirt by detergent solution.

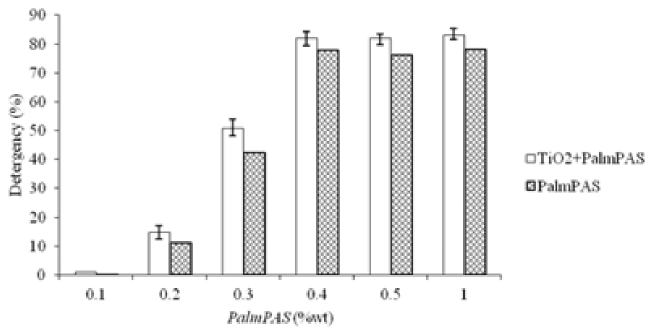

Figure 3. Detergency of dirt by the detergent

From Figure 3, it can be concluded that the higher the PalmPAS concentration, the higher the detergency. The increase in detergency is caused by the increase of surfactant to lift the MB from the cloth. Besides, there is a difference of the detergency between TiO_2-PalmPAS and PalmPAS only. TiO_2-PalmPAS has higher detergency than PalmPAS only. This phenomenon shows that TiO_2 improves the detergency of the detergent by increasing the contact surface between surfactant and dirt.

However, the detergency of this combination as shown in Fig.3 can only reach 84%. This is because mechanical energy by stirring or any other mechanical force that help the washing process was not existed. By this data, it can also be concluded that the removal of the optimum that can be done by the detergent without any mechanical aid is 84% at a concentration of 0.4 wt% PalmPAS with a certain concentration of TiO_2.

The Simultaneous Detergency and Degradation analysis is conducted by dipping a cloth that has been colored by MB into the detergent, putting into the photo-reactor for 30 minutes and giving a stirrer as mechanical energy. The results of this analysis can be seen in Figure 4.

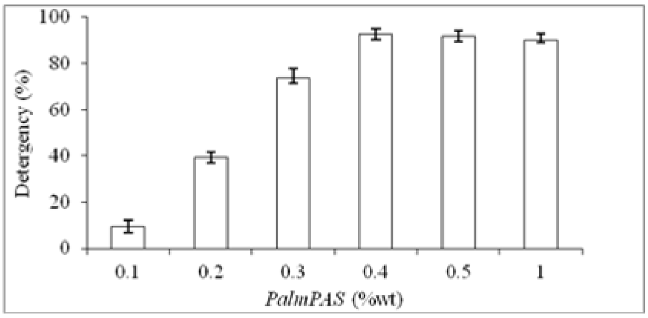

Figure 4. The Simultaneous System between Detergency and Degradation of Detergent

It can be seen that the greater the PalmPAS composition, the greater the detergency of MB as shown in Figure 4. Compared with the dipping only method, the simultaneous system method is having higher detergency. This is because PalmPAS helps TiO_2 to be well dispersed in a detergent with a hydrophilic surface binding of TiO_2. It is also expected that mechanical energy is existed by applying stirrer. The result indicates that there might be a simultaneous degradation in the clothes done by TiO_2 during washing process.

By this analysis, it is found that as same as dipping method, the more PalmPAS

concentration, the greater the detergency. However, at the PalmPAS concentrations above 0.4%, a slight decline from degradation happens because too many surfactants that hinder the contact between TiO_2 and MB, but it is not too significant. From the graph above we can then finally conclude that PalmPAS optimum concentration is 0.4% weight.

PalmPAS degradation analysis conducted by dipping a cloth that has been doped into the detergent subsequently included in a photo-reactor for 30 minutes. The data was taken from the water washing results over a certain time.

Table 2. PalmPAS Degradation

PalmPAS (wt%)	PalmPAS Concentration-0 minute (ppm)	PalmPAS Concentration-30 minute (ppm)	Degraded PalmPAS (ppm)	PalmPAS Degradation (%)
0.1	102	39	63	61
0.2	243	121	142	54
0.3	576	329	247	43
0.4	739	562	177	39
0.5	850	764	86	10

From the data in Table 2, it can be seen that the concentration of degraded PalmPAS increased by the increasing of initial PalmPAS composition. This is because the more PalmPAS in a solution, the faster TiO_2 performance in degrading the PalmPAS. However, this analysis also showed that despite the greater PalmPAS degraded, the remaining PalmPAS also getting bigger. This means that the waste that is produced by detergent in high PalmPAS concentration is high. Consequently, it can be concluded the lower PalmPAS initial concentration, the better the degradation performance.

CONCLUSIONS:

It seems clear that the combination of detergent TiO_2– PalmPAS is stable with pH treatment and stirring process. TiO_2 which precipitate after 3 hours of preparation is less than 1%, while the concentration of PalmPAS is relatively stable after 14 days of preparation. The optimum composition of the detergent in term of detergency and simultaneous detergency-degradation is 0.4%wt PalmPAS with certain TiO_2 composition. The results of detergents performance test can be seen as follows; detergency by dipping only is 84% and simultaneous detergency and degradation of MB reached 92%. Finally, the best concentration in degrading dirt is the PalmPAS with concentration of 0.4%wt.

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